PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Flexible Ionizing Radiation Shielding Material

I, STEVE SEDIAR, a cirizen of the United States of America, of 115 East 9th Street, New York, N.Y. 10003, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

by the following statement:

This invention relates to flexible radiation shielding materials comprising an elastomeric matrix material containing metal particles having ionizing radiation-absorbing charac-

teristics. Ordinarily, ionizing radiation-absorbing 15 characteristics are imparted to materials by forming them of a matrix incorporating metallic elements which have both high density and atomic number, such as lead, tungsten, uranium and the like, lead being the most 20 commonly used metal for this purpose. In order to produce such composite materials which are sufficiently flexible to form articles to be worn, such as gloves, the matrix usually consists of an elastometic material (i.e., material having rubberlike properties) such as natural or synthetic rubber, or flexible organic polymers, such as polymethane and polyvinyl chloride and the like. The metallic element is usually homogeneously dispersed through-30 out the elastomeric matrix in powder form. Even though the elastomer may be a stable compound, in many cases the addition of the metallic powder produces deleterious effects in the composite material due to the chemical 35 interaction between the two components. For example, lead powder added to natural or to some synthetic rubber latices promotes vul-canization prior to cure while in the liquid state. This occurs because the surface of each lead particle is usually covered with some lead oxide, or other lead components, obtained as a result of oxidation or chemical reaction, and

these surface films act as an accelerator agent

[Price 4s. 6d.]

to the rubber. As a result, the latex compound containing a substantial proportion of lead cannot be used for continuous production of flexible articles because the compound quickly deteriorates and becomes useless,

Heretofore, various attempts have been made to overcome this problem but none has been entirely successful. One proposal has been to coat the particles with an inert substance. However, it is extremely difficult to obtain completely uniform films surrounding each particle and coating powder in bulk tends to produce agglomeration, which materially affects the handling characteristics of the powder. Another proposal has been to reduce the chemical reactivity between the elastomer and the metal by modifying the composition of the elastomer, as by decreasing the sulphur content of the rubber. Changes made in the elastomer to accommodate the metal causes the product to be less satisfactory, and excludes the use of tried and tested elastomer compounds, particularly fast curing rubber latices. A different approach has been to use non-reactive chemical compounds of the metallic element, such as lead titanate, as the filler but this method suffers from the serious disadvantage of reducing the ionizing radiation-absorption capability of the loaded elastomeric material to as little as onefifth of the shielding possible with pure lead powder.

It is an object of the present invention to provide a new and improved flexible radiation-shielding material which overcomes the above-mentioned difficulties of the prior art.

To this end according to this invention, a flexible ionizing radiation shielding material comprises an elastomeric matrix material and filler particles distributed throughout the matrix material, the filler particles comprising an alloy, which does not cause a detrimental reaction with the elastomeric material, of ion-

surface

izing radiation-absorbing metal and at least one other metal.

Preferably the alloy contains from 0.5% to 50% by weight of the other metal or metals. Indeed the content of the other metal is preferably between 0.5% and 20% by weight.

This preferred material may be made by a method comprising alloying the ionizing 10 radiation-absorbing metal with from 0.5% to 20% by weight of at least one other metal to form an alloy which does not cause a detrimental reaction with the elastomeric material, and adding the alloy to the elasto-15 meric material in the form of small particles.

The method may include the step of dipping a form defining a flexible ionizing radiation-shielding article into a supply of the clastomer to which the alloy has been added.

Pure metals are modified both physically and chemically by addition of varying amounts of other elements to form alloys. (The term alloy refers to a combination of two or more elements which exhibit metallic 25 properties). The resulting properties of the alloy differ appreciably from those of the parent elements. Even minute amounts of an alloying element within a base metal may produce significant metallurgical changes, and 30 thereby affect the physical and chemical nature of the base material. Alloys are usually made by a solution process where at an elevated temperature the elements dissolve in each other to form a single phase. Upon cooling, the alloy may have one or more interspersed phases.

Since lead, due to its low cost, excellent radiation-absorbing characteristics for X-rays and gamma rays, and ease of powder manu-40 facture, is used extensively, the discussion which follows is devoted to lead powder, its reactivity and its use with elastomers. However, any other ionizing radiation-shielding metal which also causes problems by its 45 reactivity with elastomers can be handled

similarly Metallic lead is known to be a chemically re-active substance. When lead is freshly prepared or when cut, the lead surface is bright 50 and shiny in appearance. Upon exposure to air this surface tarnishes and becomes dull grey, due to the formation of a film of lead oxides and basic lead carbonate. Lead in contact with hard water becomes coated with 55 a film of insolvible lead salts, depending on the nature of the dissolved chemicals in the hard water. This film may contain basic lead carbonate, lead sulphate and lead phosphate. Lead in contact with distilled water or rain-60 water, which contains dissolved oxygen, is attacked to form soluble lead hydroxide. Lead in contact with many other chemicals forms various lead compounds.

As already stated, freshly manufactured 65 lead powder, though shiny in apearance at first, upon exposure to air tarnishes rapidly. If the powder is used immediately and placed in a solution or mixture which is free of all chemicals that could possibly attack the lead surface, then no surface lead compaunds would be formed. Generally, it is very difficult to obtain commercial lead powder that has not been exposed to air. Also, many applications require that certain chemicals be present in the elastomeric material for proper compounding and processing of the elasiomer. For example, sulphur is used extensively in rubbers as a vulcanizing agent and sulphur does combine with lead during the compounding process to form lead sulphide, which 80 shows up as a blackening of the material.

Many lead compounds, including lead monoxide and lead carbonate, act as accelerators for various types of rubber latices. Their presence in a rubber latex in any large quantity produces incipient vulcanization, in-creased viscosity, possible gelation and overcured articles. Experiments made with prevulcanized natural rubber latex filled with lead powder, showed that the lead compounds derived from the lead powder reacted to produce incipient vulcanization of the latex, resulting in weak and cracked products.

When the metallic powder used in a flexible ionizing radiation-shielding material is alloyed to prevent deleterious reaction with the clastomeric material in which it is to be incorporated, for example, where lead is the ionizing radiation-absorbing material, it may be alloyed with for example, tin, antimony, bismuth, barium, cadmium, or silver, separately or in combination, the alloys no longer react with the elastomeric material and, consequently, extend the por life of dipping compounds to a time commensurate with that required for continuous production processes.

The amount of alloying elements used may vary from 0.5 to 50 per cent by weight with the balance being lead. For best results, the the amount of alloying elements should be between 0.5 to 20 per cent and preferably less than ten per cent by weight. When this range is used, the dilution of lead in its radiation-absorbing characteristics is kept low. The content by weight of the radiationabsorbing alloy in the flexible material, may

be, for example, from 80 to 95 percent.

Direct comparison of lead alloys to lead compounds shows that the alloys are far radiation-shielding superior as ionizing materials. The reduction in shielding characteristics is low for alloys because the alloying elements have good radiation absorption and the amount used is small, whereas lead compounds have non-absorbing elements, such as. 125 oxygen, contained within them and these are present in large proportions. Actual measurements made with a 10 percent tin/90 percent by weight lead alloy shows only a slight difference in comparison to 100 percent lead, 130

120

and, for all practical purposes, can be considered to be solid lead insofar as radiationshielding properties are concerned.

It should be noted that, though lead has been discussed in detail, any other ionizing radiation-shielding metal may be modified similarly where reactivity in an elastomermetal composite, is found

The following ionizing radiation-absorbing 10 powders have proved satisfactory in elastomeric compositions; the percentages being by weight:-

15

 5 per cent tin/95 per cent lead
 10 per cent tin/90 per cent lead 3. 5 per cent antimony/95 per cent lead

Any one of these alloys may be used in the two examples of elastomer-metal composites described below.

EXAMPLE A.

20 Parts by Weight Prevulcanized natural subber latex 100 10% KOH solution Surface active agent 25 Lead alloy powder The natural rubber latex, No. BL-5108, was obtained from Berco Industries Corporation of Westbury, New York. The surface active agent, Darvan No. 7, was supplied by 30 R. T. Vanderbilt Company; and is a 25 per cent solution of a polymerised electrolytic material used for stabilizing the compound. The lead alloy powders used were supplied by Welded Carbide Company of Clifton, New - 35 Jersey. The 10% KOH solution and latex were first mixed together. Then the alloy powder was added and thoroughly stirred until a homogeneous dispersion was obtained. The compound was left to stand for 24 hours until all the trapped air escaped; and then the surface active agent was added. The shelf life of this mixture was about six months.

Regular porcelain forms were dipped into this compound to form gloves. Gloves made 45 with this compound had an ionizing radiation absorbance equivalent to lead sheet ranging between 0.02 to 2.0 millimetres thick, depending on the number of dips. This wide range includes most present practical applica-50 tions for gloves and similar products.

For many applications, it is desirable to apply surface coats to the dipped articles. Coating the radiation barrier material has several advantages. It increases the tensile strength and tear strength and thereby prolongs the service life of the product. Colour and texture of surfaces can be controlled. Surface coats are made by dipping the forms in unfilled latex stock at both the beginning and completion of the dipping operations. These surface coats need not be of the same latex or rubber as that used in the filled compound. Sometimes increased chemical resistance or other specific characteristics are

desired for these surface coats depending on the end use of the ionizing radiation-shielding product. Service requirement for gauntlets used in hot box applications differ from those gloves in radiological and fluoroscopic applic-

In many cases, the inside of the glove may be covered with flock to permit ease of insertion and withdrawal of hands and to give the wearer a more comfortable feel. In other cases, a thin cotton glove insert or one made of synthetic fibres is used.

The latex compound may be used also for making sheet material by spreading it on a flat stock or on a fabric. The more desirable type fabric is of an elastic-stretch type. Outer coarings may be applied to one or both sides of the flat ionizing radiation barrier material.

EXAMPLE B

	Parts by	
70.7 1 4 44 44 44 44	Weight	85
Polyvinyl chloride dispersion	resin 100	
Di (2-Ethylhexyl) Phthalate	200	
Organotin stabilizer	1	
Lead alloy powder	3,000	

The above are mechanically stirred together to form a homogenous mixture. The composition may be used with other plasticizers and stabilizers than those given. Sheets are cast on flat stock and cured in the conventional manner. Again skins of unfilled vinyl are used where added strength, colour or texture are required. Fabric may be added to one or both sides for added durability and appearance. The fabric found to be most effective is the elastic-stretch type.

The above formulations may be used to make articles of wear, such as gloves, gaunt-lets, aprons, caps and the like, and have excellent shielding characteristics for X-rays and low-energy gamma rays. Considerable 105 added flexibility and softness may be imparted to these articles by employing the method described in my specification No. 1,072,206. By this method, lower elastic modulus, higher elongation, increased flexibility and softness is imparted to the composite elastomer-metal material than is ordinarily possible by conventional methods. The method employed is essentially to have each particle housed in a cell in the elastomer material, each cell being larger than its enclosed particle

WHAT I CLAIM IS:-1. A flexible ionizing radiation-shielding material comprising an elastomeric matrix material and filler particles distributed throughout the matrix material, the filler particles comprising an alloy, which does not cause a detrimental reaction with the elastomer material, of an ionizing radiationabsorbing metal and at least one other metal. 2. A material according to claim 1, in

which the alloy contains from 0.5% to 50% by weight of the other metal or metals.

3. A material according to claim 2, in which the alloy contains from 0.5% to 20% by weight of the other metal or metals.

4. A, material according to any one of claims 1 to 3, wherein the ionizing radiation-absorbing material is lead.

5. A material according to claim 4, where-

10 in the other metal is tin.

6. A material according to claim 4, wherein the other metal is antimony.

A material according to any one of the preceding claims, wherein the elastomeric

15 matrix material is rubber.

8. A method for making flexible radiationshielding material according to claim 3, comprising alloying the ionizing radiationabsorbing metal with from 0.5% to 20% by 20 weight of at least one other metal to form an alloy which does not cause a detrimental reaction with the elastomeric material, and adding the alloy to the elastomeric material in the form of small particles.

9. A method according to claim 8, including the step of dipping a form defining a

flexible ionizing radiation-shielding article into a supply of the elastomer to which the alloy has been added.

10. A method according to claim 8 or claim 9, wherein the ionizing radiation-absorbing metal is lead and the elastomeric material is a rubber later.

11. A method according to claim 9, wherein the lead is alloyed with from 5% to 10% by weight of tin.

12. A method according to claim 3 wherein the lead is alloyed with from 5% to 10%

by weight of antimony.

13. A material according to claim 1, substantially as described herein with reference to Example A or Example B.

14. A method according to Claim 8, substantially as described herein with reference to Example A or Example B.

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